Structural Elucidation of 1,3-Phenylenebis(methylene)-Bridged Calix[6]arenes with Four Uncapped Hydroxy Groups

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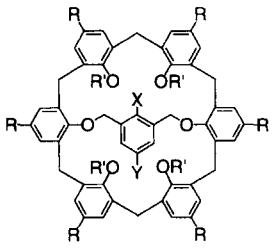
1,3-Phenylenebis(methylene)-bridged calix[6]arenes with four uncapped hydroxy groups at the lower rim and various kinds of functionalities on the bridging unit were synthesized. Their structures in solution and in the crystalline state were determined by NMR spectroscopy, molecular mechanics calculations, and X-ray crystallographic analyses. They were found to adopt a pinched cone conformation, where the bridging 1,3-phenylenebis(methylene) unit lies below in such a way that it forms the bottom of the cone. There is a strong intramolecular hydrogen bonding network forming a cyclic array in these molecules; this network is considered to play an important role in the stabilization of the pinched cone conformation. The conformational mobility of the bridging unit was also investigated. It was found that the steric demand of the central functionality has a great influence on the swinging motion of the bridging unit.

Calixarenes have been widely utilized as versatile building blocks in supramolecular chemistry.[1] While calix[4]arenes have long played a leading part in the chemistry of this series of macrocycles, calix[6]arenes bearing a cavity large enough to interact with neutral organic molecules have gained increasing attention during the last several years. This larger member of the calixarene family has a potential to be functionalized in a higher order. We have been investigating the synthesis and applications of the 1,3-phenylenebis(methylene)-bridged calix[6]arenes represented by the general formulae shown in Chart 1, where the lower rim substituent R′ is hydrogen, methyl or benzyl.[2] Similar bridged calix[6]arenes have also been described by Shinkai[3] and Lüning.[4]



1: R = *t*-Bu, R' = H
2: R = H, R' = H

Chart 1.

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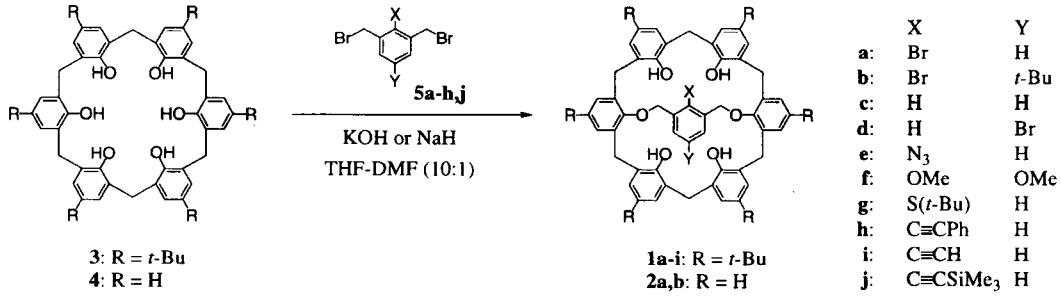
For use of these compounds as a molecular platform for subsequent synthetic elaboration, it is a prerequisite for their structural features to be fully clarified. We previously reported the conformational behavior of the bridged calix[6]arenes **1** with four uncapped hydroxy groups in a preliminary communication.[2b] Lüning et al. also described the structures of compounds **1** independently.[4e] However, there have been some disagreements between the conformations proposed by Lüning[4e] and by us[2b] as the most stable conformation of **1**. Furthermore, there has been no example of their crystallographic analysis. We describe here the full details of the structural elucidation of the tetrahydroxy compounds **1** and **2** bearing various kinds of functionalities on the bridging unit, along with some examples of crystallographic analyses.

Results and Discussion

The bridged calix[6]arenes **1a**—**h** were prepared by the reaction of *p*-*t*-butylcalix[6]arene (**3**) with 1,3-bis(bromomethyl)benzene derivatives **5a**—**h** in the presence of NaH or KOH in THF–DMF in good to high yields (Scheme 1). The results are summarized in Table 1. In the reaction of **3** with **5j**, the trimethylsilyl group was replaced by hydrogen to afford **1i** with a terminal acetylene moiety. The reaction of *p*-H-calix[6]arene (**4**) with **5a** and **5b** similarly gave the corresponding products **2a** and **2b**, respectively.

In the preliminary communication,[2b] we reported that tetrahydroxy compound **1a** with a bromo functionality has a pinched cone conformation (Chart 2a) based on the NMR study and molecular mechanics calculation with AMBER* force field. Recently, however, Lüning et al. reported that a half-pinched/half-winged cone conformation (Chart 2b) was obtained as the most stable structure of **1a** by MM3(94)



Scheme 1.

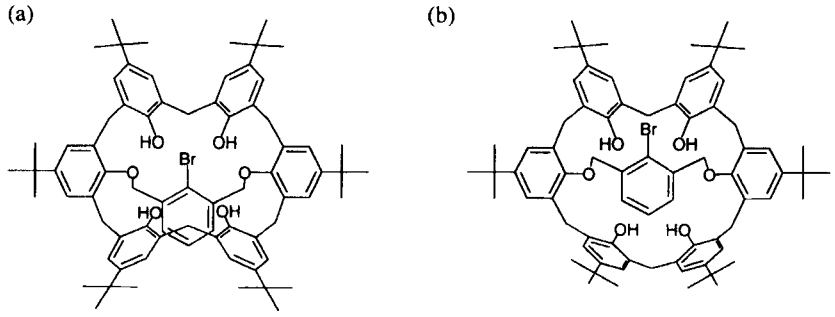


Chart 2.

Table 1. Bridging Reactions of Calix[6]arenes (**3** and **4**) with Dibromide **5**[a)]

Calixarene	5	X	Y	Product	Conditions	Yield/%
3	**5a**	Br	H	**1a**	II	89
4				**2a**	II	83
3	**5b**	Br	*t*-Bu	**1b**	II	60
4				**2b**	II	86
3	**5c**	H	H	**1c**	I	68[b)]
3	**5d**	H	Br	**1d**	I	91
3	**5e**	N_3	H	**1e**	I	86
3	**5f**	OMe	OMe	**1f**	II	73
3	**5g**	S(*t*-Bu)	H	**1g**	II	72
3	**5h**	C≡CPh	H	**1h**	II	76
3	**5j**	C≡CSiMe$_3$	H	**1i**[c)]	II	96

a) Conditions I: NaH, THF–DMF (10 : 1), reflux, 1 d. Conditions II: KOH, THF–DMF (10 : 1), room temperature, 1 d. b) 71% in Ref. 3a. c) X = C≡CH, Y = H.

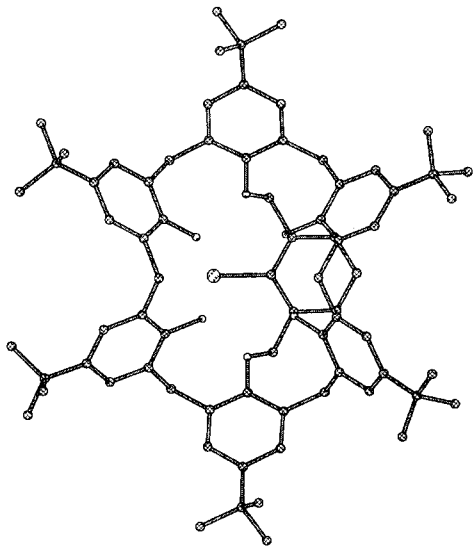


Fig. 1. Energy-minimized structure of **1a** (MM3*, GB/SA $CHCl_3$).

calculations.[4e] We performed the calculation using MM3* force field with MacroModel V6.5 program,[5] and obtained a pinched cone conformation again (Fig. 1). The half-pinched/half-winged conformation was found to be a local minimum, which is less stable by 2.8 kcal mol^{-1} than the pinched cone global minimum.

The structure of **1a** was finally established by X-ray crystallographic analysis as shown in Fig. 2. The calix[6]-arene moiety adopts a pinched cone conformation, where the macrocycle is pinched at the C_A and C_B positions, and the bridging 1,3-phenylenebis(methylene) unit lies below it in such a way that it forms the bottom of the cone. The distances between the adjacent oxygen atoms at the lower rim were found to fall between 2.69—2.80 Å (Table 2), indicating that there is a cyclic array of the intramolecular hydrogen bonding, as there is in the parent calix[6]arene **3** (vide infra). On the other hand, no intermolecular hydrogen bond was found in the crystal structure.

The molecular structure of **1a** is in excellent agreement with the result of our MM3* calculation, shown in Fig. 1. It is of note that the pinched cone conformation of the calix-[6]arene macrocycle found in the crystal structure and the lowest energy structure of **1a** has a striking resemblance to the conformation of the parent calix[6]arene **3** obtained by X-ray crystallographic analysis[6] and molecular mechanics calculation.[7] This suggests that the parent calix[6]arene **3** can be bridged by a 1,3-phenylenebis(methylene) unit without altering its conformation, which is stabilized by a cyclic array of the hydrogen bonds between the hydroxy groups. In

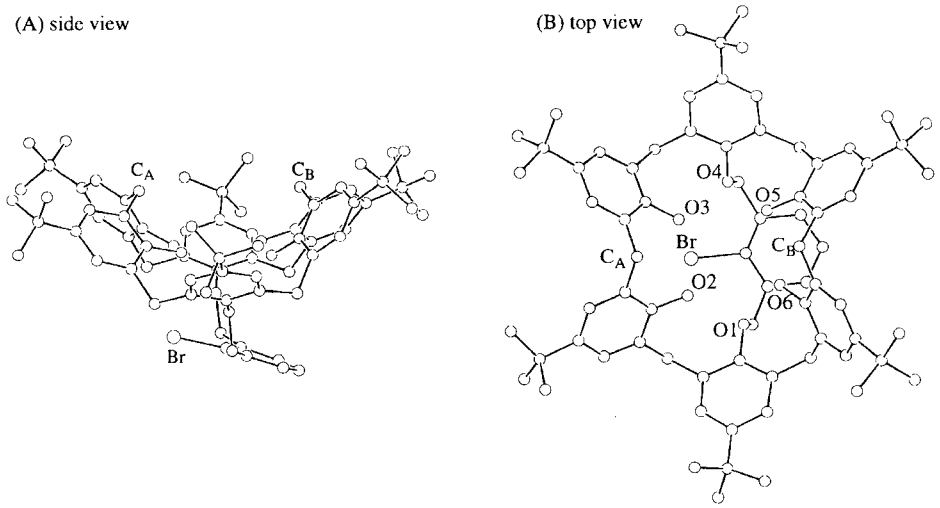


Fig. 2. Crystal structure of bridged calix[6]arene **1a**. Hydrogen atoms, disordered atoms, and solvent molecules were omitted for clarity.

Table 2. O–O Distances (Å) of the Bridged Calix[6]arenes in the Crystalline State

Compound	O1–O2	O2–O3	O3–O4	O4–O5	O5–O6	O6–O1
1a	2.772(7)	2.738(6)	2.798(5)	2.741(9)	2.687(6)	2.772(7)
1i	2.759(4)	2.729(3)	2.784(3)	2.735(5)	2.692(3)	2.838(3)
1c	2.632(2)	2.653(2)	2.937(2)	2.657(3)	2.644(2)	2.906(2)
1d	2.622(4)	2.672(4)	2.924(3)	2.644(5)	2.632(4)	2.869(4)

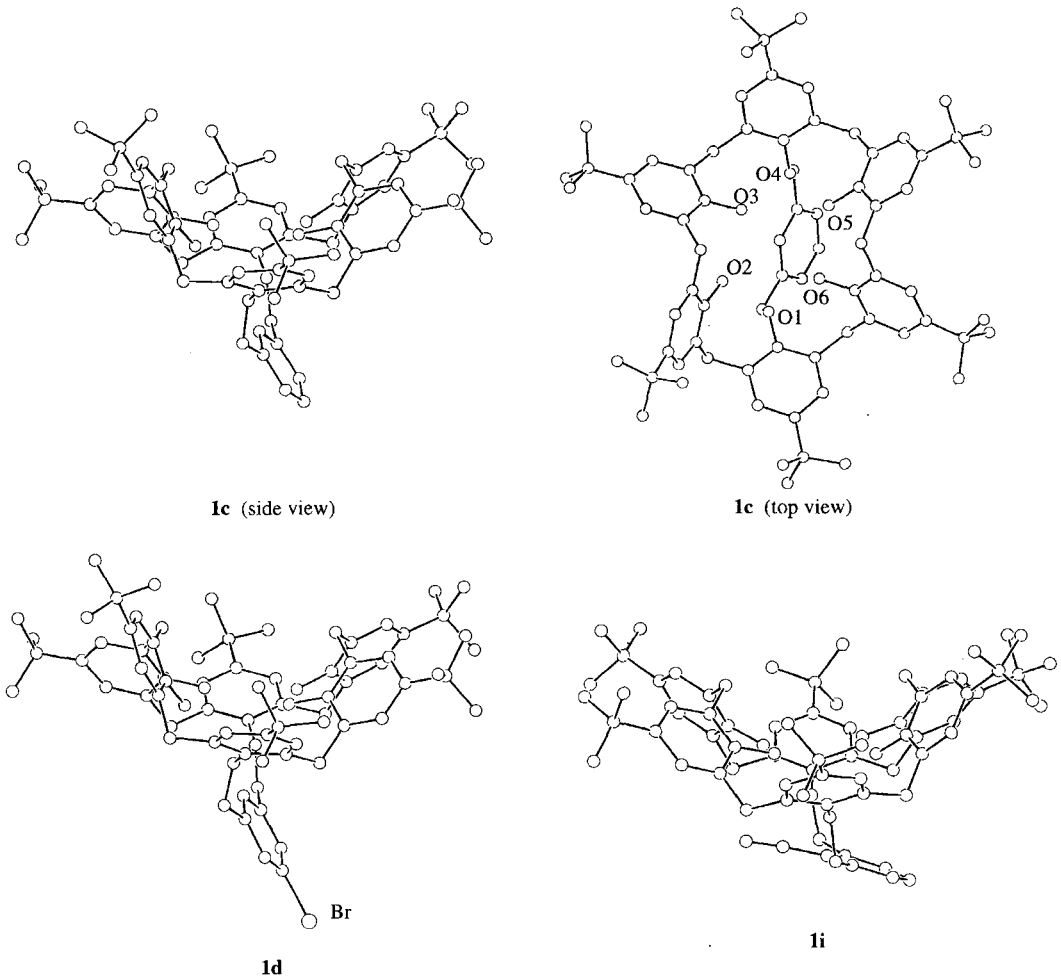
the half-pinched/half-winged conformation, the network of the hydrogen bonds is divided into two parts and hence the cyclic array is lost. This probably renders this conformation unfavorable in terms of energy.

The crystal structures of **1c**, **1d**, and **1i** were also determined by X-ray analyses (Fig. 3). It was found that all of these compounds have a pinched cone conformation similar to that of **1a**. While the conformation of the bridging unit of **1i** bearing an ethynyl functionality is essentially the same as that of **1a**, the bridging aromatic rings of **1c** and **1d** without a central functionality X are located under the calix[6]arene macrocycle with an inclination of 60.5° to the average plane of the macrocycle (defined as the least-square plane of the four oxygen atoms: O2, O3, O5, and O6). These values are considerably larger than those of **1a** (17.7°) and **1i** (19.5°) with a bromo and an ethynyl functionality, respectively. It is likely that in compounds **1a** and **1i** the network of intramolecular hydrogen bonds prevents the central functionality X on the bridging unit from staying in the cavity of calix[6]arene, whereas in compounds **1c** and **1d** the bridging aromatic ring can stand rather vertically without breaking the hydrogen bonding network.

The O–O distances of **1a**, **1c**, **1d**, and **1i** are listed in Table 2. In compounds **1a** and **1i**, the distances between the phenol oxygen atom (O2, O3, O5, and O6) and the ether oxygen atom (O1 and O4) were found to be almost the same, indicating that the protons are distributed in two ways: (a) and (b), as depicted in Scheme 2. On the other hand, there are clear differences between the distances O1–O2 and O3–O4 as well as O4–O5 and O6–O1 in compounds **1c** and **1d**. The distances O1–O2 and O4–O5 are shorter than O3–O4 and O6–O1, respectively, by 0.2—0.3 Å, indicating the contribution of the structure (a) is larger than that of (b) in the crystalline state. The slight distortion of calix[6]arene moiety found in the crystal structures of **1c** and **1d** is considered to result from this dissymmetry in the hydrogen bonding.

The ^{1}H NMR spectra ($CDCl_2CDCl_2$) of **1a** at various temperatures are shown in Fig. 4.[2b] Included among the features of the spectrum at 0 °C (Fig. 4c) are three singlets (1 : 1 : 1 ratio) which belong to three sets of *t*-butyl groups; four pairs of doublets in the ratio 1 : 1 : 2 : 2 for $ArCH_2Ar$ methylene groups, indicating that there are four kinds of $ArCH_2Ar$ groups in that ratio; one pair of doublets for $ArCH_2O$ methylenes; and two singlets for hydroxy groups. This spectral pattern is consistent with a conformation of C_s symmetry which possesses only one symmetry plane bisecting the 1,3-phenylenebis(methylene) bridge. This molecular symmetry of **1a** was corroborated by its ^{13}C NMR spectrum ($CDCl_3$, −20 °C), which showed the signals for three kinds of *t*-butyl groups, four peaks for $ArCH_2Ar$ groups, and one peak for $ArCH_2O$ groups. These results indicate that also in solution **1a** adopts a conformation similar to that in the crystalline state (Fig. 2). The results of the NOE experiments ($CDCl_3$, −40 °C) shown in Fig. 5 are consistent with that conformation. The resonances of the hydroxy protons appearing at fairly low fields also support the strong hydrogen bonding interactions.

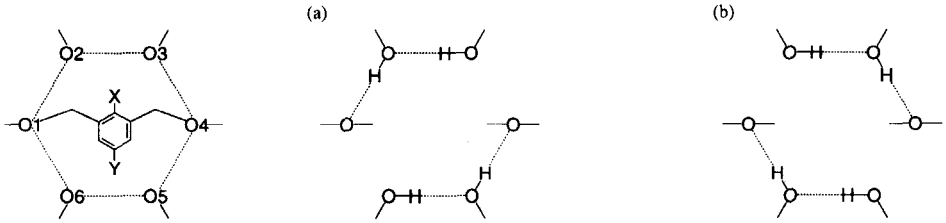
An increase in temperature up to 130 °C induced a change of the ^{1}H NMR spectra of **1a** shown in Fig. 4a.[2b] At 130 °C, the *t*-butyl resonances appeared as two singlets (1 : 2 ratio) and the hydroxy resonances became one singlet. Concomitantly, the $ArCH_2Ar$ and $ArCH_2O$ methylenes changed to two



1c (side view) **1c** (top view)

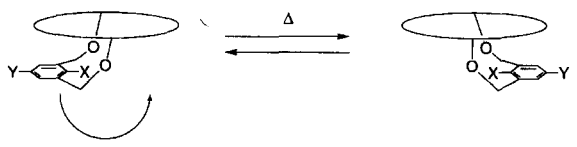
1d **1i**

Fig. 3. Crystal structures of bridged calix[6]arenes **1c**, **1d**, and **1i**. Hydrogen atoms, disordered atoms, and solvent molecules were omitted for clarity.



Scheme 2.

pairs of doublets (2 : 1 ratio) and one singlet, respectively. This spectral change induced by an increase in temperature can be explained by assuming that at high temperatures the central aromatic ring undergoes a rapid swinging motion with the bromo functionality passing through the cavity, as shown in Scheme 3, to result in the complete equivalence of the four non-bridged phenolic rings. This swinging motion of the central aromatic ring was also described by Lüning independently.[4e] From the coalescence temperature for the *t*-butyl resonances, a $\Delta G^{\ddagger}$ value of 16.3 kcal mol^{-1} was calculated for the swinging motion. The same $\Delta G^{\ddagger}$ value of 16.3 kcal mol^{-1} was also calculated from the coalescence temperature for the hydroxy resonances, although there is slight temperature-dependence of the chemical shift of the hydroxy protons. Therefore, the $\Delta G^{\ddagger}$ values for this swinging process calculated from the signals of the hydroxy protons are considered to be usable as a reasonable approximation. The geminal coupling of $ArCH_2Ar$ protons was still observed even at high temperatures, indicating that the free rotation of the central aromatic ring is still restricted on the NMR timescale.



Scheme 3.

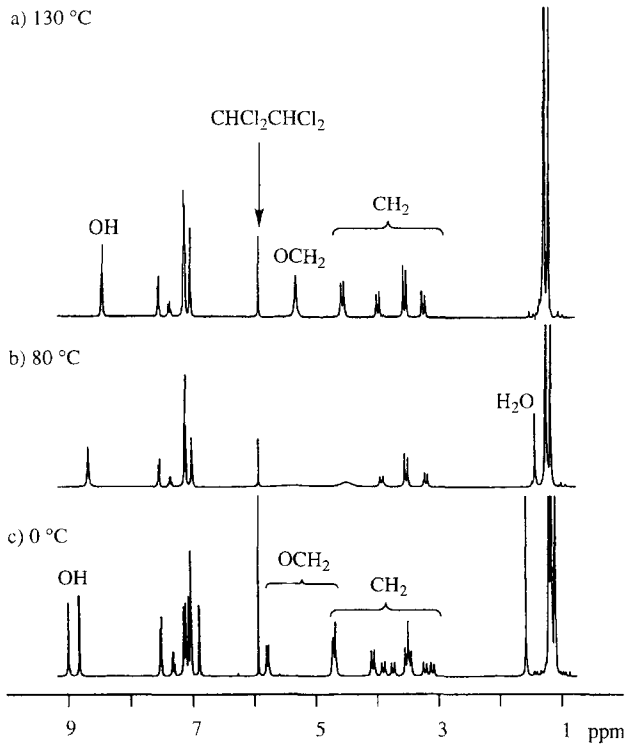


Fig. 4. ^{1}H NMR spectra of **1a** in $CDCl_2CDCl_2$ (270 MHz).

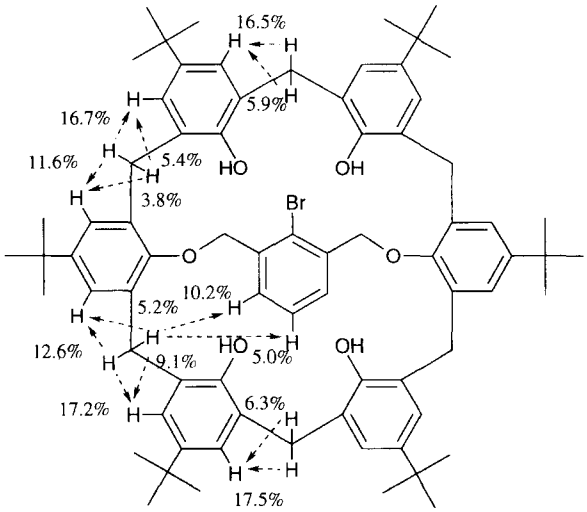


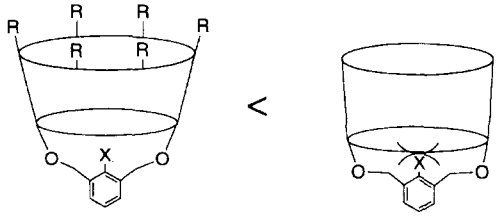
Fig. 5. Selected NOEs of **1a** (500 MHz, −40 °C, $CDCl_3$).

The effect of the upper-rim substituents on the conformational behavior was investigated by variable temperature ^{1}H NMR experiments for the bridged calix[6]arene **2a** without the *t*-butyl groups at the upper rim. Compound **2a** showed the spectral features similar to those described above for compound **1a**. At room temperature, **2a** showed a spectral pattern similar to Fig. 4c, and upon heating, the spectrum of **2a** changes to the pattern similar to Fig. 4a. This change indicates a rapid swinging motion of the bridging unit with the bromo functionality passing through the cavity; a $\Delta G^{\ddagger}$ of ca. 17.1 kcal mol^{-1}, somewhat larger than that for **1a**, was calculated from the coalescence temperature for the hydroxy resonances. This result indicates that, in compound **2a** without bulky *t*-butyl groups on the calix[6]arene macrocycle, the swinging motion of the bridging unit is more retarded than in **1a**. It may be explained by assuming that, in compound **1a**, the bulky *t*-butyl groups on the upper-rim make the cone of the calix[6]arene macrocycle more tapered off, as schematically depicted in Scheme 4, to reduce the barrier of the swinging motion of the bridging unit.

In order to investigate the effect of the substituent Y of the bridging aromatic ring on the conformational behavior, variable temperature ^{1}H NMR experiments on compound **1b** were carried out. Compound **1b** showed spectral features similar to those described above for compound **1a**. For **1b**, a $\Delta G^{\ddagger}$ of 15.5 kcal mol^{-1}, somewhat smaller than that for **1a**, was obtained. This result suggests that, in compound **1b**, the steric repulsion between the *t*-butyl group as Y and the calix[6]arene macrocycle destabilizes the ground state of the molecule in comparison with **1a**, while it has little influence on the transition state of the swinging motion, thus leading to a smaller value of $\Delta G^{\ddagger}$ for that process.

The ^{1}H NMR spectra at various temperatures of **1e**[2a] and **1f** bearing an azido and a methoxy functionality at the X position, respectively, resemble those of their bromo analog **1a** in general detail. However, the $\Delta G^{\ddagger}$ values for the swinging motion of the bridging unit were found to be 15.3 and 13.6 kcal mol^{-1} for **1e** and **1f**, respectively, indicating that the swinging motion of the bridging unit is less retarded than in **1a**, for which $\Delta G^{\ddagger}$ is 16.3 kcal mol^{-1}. This is probably because of the reduced steric demand of the azido and methoxy groups compared with that of the bromo functionality. In these tetrahydroxy compounds, the steric hindrance arising from the functional group X on the bridging unit is considered to be effective in restraining the 1,3-phenylenebis(methylene) bridging unit from undergoing the swinging motion. Lüning et al. also reported that the $\Delta G^{\ddagger}$ values of the swinging motion of the tetrahydroxy compounds bearing nitro, cyano, chloro, and iodo functionalities at the X position are 13—18 kcal mol^{-1} depending on the steric demand of the functionality.[4e] Compound **1c** without a functionality at the X position was not reported to show coalescence until −44 °C in CD_2Cl_2, indicating that the $\Delta G^{\ddagger}$ value is less than 11.4 kcal mol^{-1}. Such conformational behavior of **1c** is reasonable in terms of its C_{2v}-like structure in the crystalline state (Fig. 3).

In the ^{1}H NMR spectrum at room temperature, compounds **1g** and **1h** bearing a *t*-butylthio and a phenylethynyl functionality, respectively, showed essentially the same pattern as that of **1a**, which indicates the C_s symmetry of the molecule. It is of note, however, that in the cases of **1g** and **1h** this



Scheme 4.

pattern did not change at temperatures up to 150 °C. These results indicate that the swinging motion of the bridging unit of **1g** and **1h** is suppressed even at such high temperatures and the molecule is frozen in the conformation of C_s symmetry on the NMR timescale. Such conformational rigidity of **1g** and **1h** in comparison with their bromo analog **1a** obviously results from the large steric demand of the central functionality X.

Conclusion

A series of 1,3-phenylenebis(methylene)-bridged calix[6]-arenes with four uncapped hydroxy groups have been synthesized and their structural features have been investigated by different techniques, including NMR spectroscopy, molecular mechanics calculation, and X-ray analysis. It has been found that the tetrahydroxy compounds **1** have a strong tendency to adopt the structure where the calix[6]arene macrocycle has a pinched cone conformation. The bridging 1,3-phenylenebis(methylene) unit lies below the macrocycle in such a way that it forms the bottom of the cone, and the angle between the bridging aromatic ring and the average plane of the macrocycle varies depending on the bulkiness of the functionality X. There is a strong intramolecular hydrogen bonding network forming a cyclic array in these molecules, which is considered to play an important role in the stabilization of the above-mentioned pinched cone conformation. It has also been demonstrated that the steric demand of the central functionality X exerts a great influence on the conformational mobility of these molecules. While the central aromatic ring of **1a**—**f** and **1i** undergoes the swinging motion with an activation barrier which depends on the size and shape of the functionality X, compounds **1g** and **1h** with a *t*-butylthio and a phenylethynyl functionality, respectively, have been found to sit still in the above-mentioned conformation on the NMR timescale.

Experimental

Melting points were determined on a Yanaco micro melting point apparatus. All melting points are uncorrected. THF was purified by distillation from sodium diphenylketyl under argon atmosphere before use. Dichloromethane and carbon tetrachloride were distilled from calcium hydride. Diethylamine was dried over KOH pellets before use. DMF (special grade) was purchased from Wako Pure Chemical Industries Ltd. and was used without purification. Acetone and ethanol (technical grade) were used without purification. Column chromatography and preparative TLC were carried out with Wakogel C-200 and Merck Kieselgel 60PF254 Art. 7747, respectively. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500, a JEOL JNM-A500, or a JEOL EXcalibur270 spectrometer. Assignments of NMR signals were based on 2D-COSY, HMQC, and HMBC spectra. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, the University of Tokyo.

Materials. The preparations of 5,11,17,23,29,35-hexa-*t*-butylcalix[6]arene-37,38,39,40,41,42-hexol (**3**),[8] calix[6]arene-37,38,39,40,41,42-hexol (**4**),[9] 2-bromo-1,3-bis(bromomethyl)benzene (**5a**),[10] 2-bromo-1,3-bis(bromomethyl)-5-*t*-butylbenzene (**5b**),[11] 1-bromo-3,5-bis(bromomethyl)benzene (**5d**),[12] 1,3-bis(bromomethyl)-2,5-dimethoxybenzene (**5f**),[13] 1,3-bis(bromomethyl)-2-(phenylethynyl)benzene (**5h**),[14] and 5,11,17,23,29,35-hexa-*t*-butyl-37,40-[1,3-phenylenebis(methyleneoxy)]calix[6]arene-38,39,41,42-tetrol (**1c**)[3a] have been described in the literature.

Preparation of 2-Azido-1,3-bis(bromomethyl)benzene (5e). A mixture of 2-azido-1,3-dimethylbenzene[15] (2.94 g, 20 mmol), *N*-bromosuccinimide (7.83 g, 44 mmol), and benzoyl peroxide (100 mg, 0.4 mmol) in benzene (20 mL) was refluxed for 5 h. After the addition of water, the mixture was extracted with ether and the organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel (hexane) to afford colorless crystals of **5e** (4.08 g, 67%).

5e: Colorless crystals, mp 40—41 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.58 (s, 4H), 7.18 (t, J = 7.7 Hz, 1H), 7.35 (d, J = 7.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 28.69 (t), 126.53 (d), 131.70 (d), 132.84 (s), 137.05 (s); IR (KBr) $\nu(N_3)$ 2116 cm^{-1}. Found: C, 31.45; H, 2.30; Br, 52.47; N, 13.80%. Calcd for $C_8H_7Br_2N_3$: C, 31.51; H, 2.31; Br, 52.40; N, 13.78%.

Preparation of 1,3-Bis(bromomethyl)-2-*t*-butylthiobenzene (5g). A mixture of *N*-bromosuccinimide (3.13 g, 17.6 mmol) and 2-*t*-butylthio-1,3-dimethylbenzene[16] (1.56 g, 8.03 mmol) in carbon tetrachloride (16 ml) was irradiated by a 400 W high pressure mercury lamp for 5 h in a water bath and then the precipitates were filtered off. The solvent was removed from the filtrate and the residue was subjected to chromatography (SiO_2/hexane) to give colorless crystals of **5g** (1.54 g, 57%).

5g: Colorless crystals, mp 93—94 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.30 (s, 9H), 4.95 (brs, 4H), 7.37 (t, J = 7.7 Hz, 1H), 7.58 (d, J = 7.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 31.5 (q), 33.3 (t), 49.2 (s), 129.8 (d), 131.2 (s), 131.3 (d), 144.6 (s). Found: C, 41.20; H, 4.61; Br, 45.83; S, 9.18%. Calcd for $C_{12}H_{16}Br_2S$: C, 40.93; H, 4.58; Br, 45.38; S, 9.11%.

Preparation of (2,6-Dimethylphenylethynyl)trimethylsilane. To a solution of 2-iodo-1,3-dimethylbenzene[17] (4.65 g, 20 mmol), copper(I) iodide (100 mg, 0.52 mmol), and ethynyltrimethylsilane (4.2 mL, 30 mmol) in diethylamine (25 mL) was added tetrakis(triphenylphosphine)palladium (300 mg, 0.26 mmol) and the mixture was stirred at 50 °C for 24 h. After removal of the solvent and addition of water, the mixture was extracted with chloroform. The extract was dried over $MgSO_4$ and the solvent was evaporated to give crude products, chromatography of which on silica gel (hexane) afforded a colorless liquid (3.72 g, 92%) with enough purity for the next reaction. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.26 (s, 9H), 2.42 (s, 6H), 7.01 (d, J = 7.5 Hz, 2H), 7.09 (t, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 0.16 (q), 20.99 (q), 102.76 (s), 102.81 (s), 112.97 (s), 126.55 (d), 127.80 (d), 140.63 (s).

Preparation of [2,6-Bis(bromomethyl)phenylethynyl]trimethylsilane (5j). A mixture of (2,6-dimethylphenylethynyl)-trimethylsilane (1.0 g, 5.0 mmol), *N*-bromosuccinimide (3.13 g, 18 mmol), and benzoyl peroxide (100 mg, 0.4 mmol) in carbon tetrachloride (10 mL) was refluxed for 7 h. After filtration of succinimide and removal of the solvent, the residue was chromatographed on silica gel (hexane) to afford colorless crystals of **5j** (620 mg, 34%).

5j: Colorless crystals; mp 50—52 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.35 (s, 9H), 4.67 (s, 4H), 7.23 (t, J = 7.7 Hz, 1H), 7.34 (d, J = 7.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = −0.29 (q), 31.57 (t), 98.63 (s), 107.37 (s), 122.81 (s), 128.74 (d), 129.54 (d), 140.27 (s). Found: C, 43.16; H, 4.37; Br, 44.18%. Calcd for $C_{13}H_{16}Br_2Si$: C, 43.35; H, 4.48; Br, 44.37%.

37,40-[5-Bromo-1,3-phenylenebis(methyleneoxy)]-5,11,17,23,29,35-hexa-*t*-butylcalix[6]arene-38,39,41,42-tetrol (1d). To a suspension of sodium hydride (60% in oil, 240 mg, 6 mmol) in THF (5 mL) was added a solution of *p*-*t*-butylcalix[6]arene (**3**) (973 mg,

1.0 mmol) in THF (85 mL) and DMF (10 mL). After the mixture was stirred at room temperature for 2 h, a solution of dibromide **5d** (343 mg, 1.0 mmol) in THF (10 mL) was added dropwise at room temperature, and the reaction mixture was refluxed for 24 h. After addition of water, the mixture was poured into **1** M aq HCl (1 M = 1 mol dm^{-3}), extracted with chloroform, dried over $MgSO_4$, and evaporated to dryness. Chromatographic separation on silica gel (hexane/chloroform, 1 : 1) followed by recrystallization (chloroform/methanol) afforded the bridged calix[6]arene **1d** (1.05 g, 91%).

1d: Colorless crystals, mp 240 °C (decomp); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.20 (s, 18H), 1.27 (s, 36H), 3.33 (d, J = 13.6 Hz, 2H), 3.50 (d, J = 13.4 Hz, 4H), 4.18 (d, J = 13.6 Hz, 2H), 4.27 (d, J = 13.4 Hz, 4H), 5.23 (s, 4H), 7.11 (s, 8H), 7.13 (s, 4H), 7.29 (s, 2H), 8.46 (s, 1H), 8.90 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 31.29 (q), 31.64 (q), 32.89 (t), 33.07 (t), 33.91 (s), 34.28 (s), 76.14 (t), 121.80 (s), 122.04 (d), 125.26 (d), 125.98 (d), 126.47 (d), 127.19 (s), 127.57 (s), 128.48 (d), 132.18 (s), 140.34 (s), 142.71 (s), 148.09 (s), 149.80 (s), 149.82 (s). Found: C, 74.88; H, 7.45%. Calcd for $C_{74}H_{89}BrO_6 \cdot 2H_2O$: C, 74.66; H, 7.87%.

37,40-[2-Azido-1,3-phenylenebis(methyleneoxy)]-5,11,17,23,29,35-hexa-*t*-butylcalix[6]arene-38,39,41,42-tetrol (1e). To a suspension of NaH (60% in oil, 2.46 g, 62 mmol) in THF (5 ml) was added a suspension of **3** (2.92 g, 3.0 mmol) in THF (70 ml) and DMF (10 ml). After the mixture was stirred at room temperature for 2 h, a solution of **5e** (920 mg, 3.0 mmol) in THF (25 ml) was added dropwise at room temperature, and the reaction mixture was refluxed for 1 d. After addition of water, the mixture was poured into 1 M aq HCl, extracted with chloroform, and the organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was subjected to chromatography (silica gel, hexane/chloroform, 1 : 1) to give **1e** (2.88 g, 86%).

1e: Colorless crystals, mp 179—189 °C (decomp); ^{1}H NMR (270 MHz, $CDCl_3$, −40 °C) δ = 1.19 (s, 18H), 1.22 (s, 18H), 1.29 (s, 18H), 3.20 (d, J = 13.5 Hz, 1H), 3.33 (d, J = 13.5 Hz, 1H), 3.52 (d, J = 13.0 Hz, 2H), 3.62 (d, J = 13.2 Hz, 2H), 3.96 (d, J = 13.5 Hz, 1H), 4.11 (d, J = 13.0 Hz, 2H), 4.15 (d, J = 13.5 Hz, 1H), 4.74 (d, J = 10.9 Hz, 2H), 4.88 (d, J = 13.2 Hz, 2H), 5.95 (d, J = 10.9 Hz, 2H), 7.00—7.23 (m, 13H), 7.48 (d, J = 7.6 Hz, 2H), 8.80 (s, 2H), 9.18 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$, −40 °C) δ = 31.1 (q), 31.5 (q×2), 32.9 (t×3), 33.2 (t), 33.7 (s), 33.8 (s), 34.2 (s), 75.4 (t), 125.0 (d), 125.6 (d), 125.7 (d×2), 125.9 (d×2), 126.4 (s), 126.4 (d), 126.55 (s), 126.60 (s), 126.8 (s), 131.0 (s), 131.2 (s), 132.7 (s), 132.9 (d), 138.6 (s), 141.7 (s), 141.9 (s), 147.6 (s), 149.6 (s), 149.7 (s), 149.9 (s). IR (KBr) ν(N_3) 2137 (s) cm^{-1}. Found: C, 78.54; H, 7.81; N, 3.77%. Calcd for $C_{74}H_{89}N_3O_6 \cdot H_2O$: C, 78.34; H, 8.08; N, 3.70%.

General Procedure for the Preparation of the Bridged Calix[6]arenes 1a, 1b, and 1f—i. To a suspension of potassium hydroxide (85%, 330 mg, 5 mmol) and *p-t*-butylcalix[6]arene (**3**) (245 mg, 0.25 mmol) in THF (90 mL) and DMF (10 mL), which was stirred at room temperature for 1 h, was added a solution of the appropriate dibromide **5** (0.25 mmol) in THF (10 mL) and the mixture was stirred at room temperature for 24 h. After removal of the solvent, the residue was treated with aq NH_4Cl and extracted with chloroform. The solution was dried over $MgSO_4$ and evaporated to dryness. The residue was purified by chromatography, if necessary, and recrystallized from chloroform/methanol to afford the bridged calixarenes **1**.

37,40-[2-Bromo-1,3-phenylenebis(methyleneoxy)]-5,11,17,23,29,35-hexa-*t*-butylcalix[6]arene-38,39,41,42-tetrol (1a). Prepared from **5a** in 89% yield; colorless crystals; mp 253—257 °C (decomp); ^{1}H NMR (270 MHz, $CDCl_3$, −20 °C) δ = 1.19 (s, 18H), 1.24 (s, 18H), 1.28 (s, 18H), 3.25 (d, J = 13.7 Hz, 1H), 3.29 (d, J = 14.4 Hz, 1H), 3.54 (d, J = 13.4 Hz, 2H), 3.59 (d, J = 13.4 Hz, 2H), 3.98 (d, J = 13.7 Hz, 1H), 4.14 (d, J = 14.4 Hz, 1H), 4.19 (d, J = 13.4 Hz, 2H), 4.78 (d, J = 9.9 Hz, 2H), 4.82 (d, J = 13.4 Hz, 2H), 5.87 (d, J = 9.9 Hz, 2H), 7.02—7.17 (m, 12H), 7.32 (t, J = 7.6 Hz, 1H), 7.55 (d, J = 7.6 Hz, 2H), 8.68 (s, 2H), 8.84 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$, −20 °C) δ = 31.2 (q), 31.6 (q×2), 32.5 (t), 33.0 (t), 33.2 (t), 33.5 (t), 33.77 (s), 33.84 (s), 34.2 (s), 78.8 (t), 125.2 (d), 125.5 (d), 125.7 (d), 125.85 (d), 125.88 (d), 126.3 (d), 126.5 (s), 126.6 (s), 127.0 (s), 127.6 (s), 127.7 (s), 128.0 (d), 132.0 (s), 132.3 (d), 133.0 (s), 137.9 (s), 141.8 (s), 142.3 (s), 147.6 (s), 149.7 (s), 149.8 (s), 149.9 (s). Found: C, 76.19; H, 7.81; Br, 7.10%. Calcd for $C_{74}H_{89}BrO_6 \cdot 0.5H_2O$: C, 76.40; H, 7.80; Br, 6.87%.

37,40-[2-Bromo-5-*t*-butyl-1,3-phenylenebis(methyleneoxy)]-5,11,17,23,29,35-hexa-*t*-butylcalix[6]arene-38,39,41,42-tetrol (1b). Prepared from **5b** in 60% yield; colorless crystals; mp > 300 °C; ^{1}H NMR (270 MHz, $CDCl_3$, −20 °C) δ = 1.19 (s, 18H), 1.23 (s, 18H), 1.26 (s, 9H), 1.28 (s, 18H), 3.21 (d, J = 14.0 Hz, 1H), 3.28 (d, J = 13.5 Hz, 1H), 3.52 (d, J = 13.2 Hz, 2H), 3.58 (d, J = 14.2 Hz, 2H), 3.95 (d, J = 14.0 Hz, 1H), 4.12 (d, J = 13.5 Hz, 1H), 4.22 (d, J = 13.2 Hz, 2H), 4.76 (d, J = 9.7 Hz, 2H), 4.84 (d, J = 14.2 Hz, 2H), 5.85 (d, J = 9.7 Hz, 2H), 6.97—7.15 (m, 12H), 7.58 (s, 2H), 8.69 (s, 2H), 8.86 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$, −20 °C) δ = 31.0 (q), 31.2 (q), 31.6 (q×2), 32.5 (t), 33.10 (t), 33.14 (t), 33.6 (t), 33.77 (s), 33.84 (s), 34.2 (s), 34.5 (s), 79.2 (t), 124.2 (s), 125.1 (d), 125.5 (d), 125.67 (d), 125.72 (d), 125.8 (d), 126.3 (d), 126.4 (s), 126.9 (s), 127.1 (s), 127.6 (s), 129.5 (d), 132.4 (s), 133.0 (s), 137.2 (s), 141.6 (s), 142.2 (s), 147.6 (s), 149.7 (s), 149.8 (s), 149.9 (s), 150.7 (s). Found: C, 76.66; H, 7.99; Br, 6.41%. Calcd for $C_{78}H_{97}BrO_6 \cdot 0.5H_2O$: C, 76.82; H, 8.10; Br, 6.55%.

5,11,17,23,29,35-Hexa-*t*-butyl-37,40-[2,5-dimethoxy-1,3-phenylenebis(methyleneoxy)]calix[6]arene-38,39,41,42-tetrol (1f). Prepared from **5f** in 88% yield; colorless crystals, mp 212—215 °C; ^{1}H NMR (270 MHz, $CDCl_3$, −50 °C) δ = 1.20 (s, 18H), 1.23 (s, 18H), 1.29 (s, 18H), 3.21 (d, J = 13.5 Hz, 1H), 3.31 (d, J = 13.8 Hz, 1H), 3.49 (d, J = 13.8 Hz, 2H), 3.63 (d, J = 12.8 Hz, 2H), 3.83 (s, 3H), 3.96 (s, 3H), 4.04 (d, J = 13.5 Hz, 1H), 4.15 (d, J = 13.0 Hz, 2H), 4.23 (d, J = 13.8 Hz, 1H), 4.58 (d, J = 10.0 Hz, 2H), 4.65 (d, J = 12.8 Hz, 2H), 5.83 (d, J = 10.0 Hz, 2H), 6.91 (s, 2H), 7.03 (brd, 2H), 7.08 (brd, 2H), 7.12 (brd, 2H), 7.14 (brd, 2H), 7.15 (brd, 2H), 7.20 (brd 2H), 8.99 (s, 2H), 9.06 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$, −50 °C) δ = 31.15 (q), 31.49 (q×2), 32.66 (t), 32.83 (t), 33.09 (t), 33.19 (t), 33.69 (s), 33.81 (s), 34.14 (s), 55.29 (q), 60.97 (q), 75.36 (t), 116.61 (d), 125.10 (d), 125.22 (d), 125.54 (d), 125.64 (d), 125.73 (d), 126.16 (d), 126.64 (s), 126.69 (s), 127.16 (s), 127.45 (s), 131.34 (s), 131.83 (s), 132.84 (s), 141.58 (s), 141.95 (s), 147.14 (s), 149.71 (s), 149.84 (s), 150.14 (s), 153.11 (s), 154.49 (s). Found: C, 79.42; H, 8.25%. Calcd for $C_{76}H_{94}O_8 \cdot H_2O$: C, 79.13; H, 8.39%.

5,11,17,23,29,35-Hexa-*t*-butyl-37,40-[2-*t*-butylthio-1,3-phenylenebis(methyleneoxy)]calix[6]arene-38,39,41,42-tetrol (1g). Prepared from **5g** in 72% yield; colorless crystals, mp 198—202 °C (decomp); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.19 (s, 18H), 1.21 (s, 9H), 1.23 (s, 18H), 1.28 (s, 18H), 3.17 (d, J = 13.7 Hz, 1H), 3.25 (d, J = 13.7 Hz, 1H), 3.49 (d, J = 13.0 Hz, 2H), 3.53 (d, J = 13.1 Hz, 2H), 3.90 (d, J = 13.7 Hz, 1H), 4.06 (d, J = 13.7 Hz, 1H), 4.29 (d, J = 13.0 Hz, 2H), 4.66 (d, J = 8.8 Hz, 2H), 5.01 (d, J = 13.1 Hz, 2H), 6.27 (d, J = 8.8 Hz, 2H,), 6.99—7.15 (m, 12H), 7.40 (t, J = 7.6 Hz, 1H), 7.68 (d, J = 7.6 Hz, 2H), 8.76 (s, 2H), 8.96 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 31.29 (q), 31.33 (q), 31.65

(q), 31.69 (q), 32.9 (t), 33.3 (t), 33.6 (t), 33.8 (t), 33.8 (s), 33.9 (s), 34.2 (s), 48.4 (s), 78.8 (t), 125.2 (d), 125.3 (d), 125.6 (d), 126.0 (d), 126.06 (d), 126.13 (d), 126.8 (s), 127.0 (s), 127.4 (s), 127.8 (s), 129.9 (d), 132.5 (s), 132.5 (d), 133.6 (s×2), 141.8 (s), 142.0 (s), 144.1 (s), 147.6 (s), 150.17 (s), 150.23 (s), 150.3 (s). Found: C, 79.93; H, 8.50; S, 2.77%. Calcd for $C_{78}H_{98}O_6S\cdot 0.5H_2O$: C, 79.89; H, 8.51; S, 2.73%.

5,11,17,23,29,35-Hexa-*t*-butyl-37,40-[2-phenylethynyl-1,3-phenylenebis(methyleneoxy)]calix[6]arene-38,39,41,42-tetrol (1h). Prepared from **5h** in 76% yield; colorless crystals, mp 259—262 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.17 (s, 18H), 1.25 (s, 18H), 1.26 (s, 18H), 3.22 (d, J = 13.7 Hz, 1H), 3.23 (d, J = 13.7 Hz, 1H), 3.31 (d, J = 13.4 Hz, 2H), 3.51 (d, J = 13.0 Hz, 2H), 3.98 (d, J = 13.7 Hz, 1H), 4.03 (d, J = 13.7 Hz, 1H), 4.28 (d, J = 13.0 Hz, 2H), 4.69 (d, J = 13.4 Hz, 2H), 4.74 (d, J = 9.5 Hz, 2H), 6.04 (d, J = 9.5 Hz, 2H), 6.52 (t, J = 7.6 Hz, 2H), 6.70 (d, J = 7.6 Hz, 2H), 6.82 (d, J = 2.3 Hz, 2H), 6.83 (t, J = 7.6 Hz, 1H), 7.018 (d, J = 2.4 Hz, 2H), 7.022 (d, J = 2.4 Hz, 2H), 7.07 (d, J = 2.3 Hz, 2H), 7.09 (d, J = 2.4 Hz, 2H), 7.13 (d, J = 2.4 Hz, 2H), 7.35 (t, J = 7.6 Hz, 1H), 7.58 (d, J = 7.6 Hz, 2H), 8.66 (s, 2H), 8.85 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 31.29 (q), 31.65 (q), 31.69 (q), 32.31 (t), 33.22 (t), 33.56 (t), 33.75 (t), 33.83 (s×2), 34.22 (s), 77.58 (t), 86.39 (s), 97.42 (s), 121.89 (s), 124.94 (d), 125.25 (d), 125.41 (d), 125.94 (d), 125.97 (d), 126.21 (d), 126.79 (s), 127.09 (s), 127.15 (s), 127.18 (d), 127.59 (s), 127.74 (d), 128.82 (d), 131.06 (d), 131.34 (d), 132.20 (s), 133.33 (s), 139.56 (s), 141.91 (s), 142.20 (s), 147.63 (s), 149.99 (s), 150.19 (s), 150.37 (s). Found: C, 82.69; H, 8.04%. Calcd for $C_{82}H_{94}O_6\cdot H_2O$: C, 82.51; H, 8.11%.

5,11,17,23,29,35-Hexa-*t*-butyl-37,40-[2-ethynyl-1,3-phenylenebis(methyleneoxy)]calix[6]arene-38,39,41,42-tetrol (1i). Prepared from **5j** in 96% yield; colorless crystals, mp 245 °C (decomp); ^{1}H NMR (270 MHz, $CDCl_3$, −20 °C) δ = 1.19 (s, 18H), 1.23 (s, 18H), 1.28 (s, 18H), 3.21 (d, J = 13.7 Hz, 1H), 3.27 (d, J = 13.6 Hz, 1H), 3.47 (s, 1H), 3.52 (d, J = 13.0 Hz, 2H), 3.57 (d, J = 13.3 Hz, 2H), 3.98 (d, J = 13.7 Hz, 1H), 4.15 (d, J = 13.6 Hz, 1H), 4.18 (d, J = 13.0 Hz, 2H), 4.72 (d, J = 9.6 Hz, 2H), 4.80 (d, J = 13.3 Hz, 2H), 5.96 (d, J = 9.6 Hz, 2H), 7.01 (d, J = 2.3 Hz, 2H), 7.09 (s, 4H), 7.11—7.16 (m, 6H), 7.36 (t, J = 7.5 Hz, 1H), 7.53 (d, J = 7.5 Hz, 2H), 8.77 (s, 2H), 8.90 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$, −20 °C) δ = 31.20 (q), 31.56 (q×2), 32.69 (t), 32.91 (t), 33.23 (t), 33.49 (t), 33.75 (s), 33.86 (s), 34.18 (s), 77.38 (t), 80.76 (d), 86.71 (s), 123.76 (s), 125.16 (d), 125.34 (d), 125.60 (d), 125.82 (d), 125.85 (d), 126.24 (d), 126.57 (s), 126.69 (s), 127.28 (s), 127.93 (s), 129.18 (d), 130.65 (d), 131.97 (s), 133.05 (s), 140.08 (s), 141.77 (s), 142.13 (s), 147.43 (s), 149.54 (s), 149.91 (s), 150.15 (s). Found: C, 81.39; H, 8.06%. Calcd for $C_{76}H_{90}O_6\cdot H_2O$: C, 81.68; H, 8.30%.

37,40-[2-Bromo-1,3-phenylenebis(methyleneoxy)]calix[6]-arene-38,39,41,42-tetrol (2a). To a suspension of potassium hydroxide (85%, 1.32 g, 20 mmol) in THF (30 ml) was added a solution of **4** (637 mg, 1.0 mmol) in THF (270 ml) and DMF (40 ml). After this mixture was stirred at room temperature for 1.5 h, a solution of **5a** (343 mg, 1.0 mmol) in THF (100 ml) was added dropwise at room temperature, and the reaction mixture was stirred at room temperature for 24 h. After addition of water, the mixture was concentrated until most of THF was removed. The residue was poured into 1 M aq HCl, extracted with chloroform, and the organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was separated by chromatography (SiO_2/$CHCl_3$) to give **2a** (680 mg, 83%).

2a: Colorless crystals (from dichloromethane/ethanol), mp > 300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.22 (d, J = 13.8 Hz, 1H), 3.31 (d, J = 13.7 Hz, 1H), 3.55 (d, J = 13.2 Hz, 2H), 3.62 (d, J = 13.4 Hz, 2H), 3.92 (d, J = 13.8 Hz, 1H), 4.09 (d, J = 13.7 Hz, 1H), 4.20 (d, J = 13.2 Hz, 2H), 4.77 (d, J = 9.8 Hz, 2H), 4.88 (d,

Table 3. Crystallographic Data for **1a**, **1c**, **1d**, and **1i**

	1a·5$CHCl_3$	**1i**·5$CHCl_3$	**1c**·$CH_3CN\cdot C_6H_6$	**1d**·$CH_3CN\cdot C_6H_6$
Formula	$C_{79}H_{94}BrCl_{15}O_6$	$C_{81}H_{95}Cl_{15}O_6$	$C_{82}H_{99}NO_6$	$C_{82}H_{98}BrNO_6$
Temperature/K	150	120	120	120
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/a$	$P2_1/a$
a/Å	16.022(2)	15.971(1)	17.965(1)	18.014(1)
b/Å	17.403(2)	17.359(1)	23.652(1)	23.970(2)
c/Å	17.491(2)	17.526(1)	18.081(1)	18.184(1)
α/deg	63.310(5)	63.545(3)		
β/deg	79.249(6)	79.228(3)	110.920(2)	112.643(4)
γ/deg	79.050(6)	79.201(2)		
V/Å^3	4249.5(8)	4243.4(5)	7176.3(6)	7246.6(8)
Z	2	2	4	4
Calculated density/g cm^{-3}	1.369	1.328	1.106	1.167
Reflections collected	26668	27129	48315	43191
Unique	14302	14573	13461	13376
R_{int}	0.029	0.021	0.027	0.037
F_{000}	1812	1768	2584	2720
Limiting indices	$0 \le h \le 19$	$0 \le h \le 19$	$0 \le h \le 21$	$0 \le h \le 21$
	$-20 \le k \le 21$	$-20 \le k \le 21$	$0 \le k \le 28$	$0 \le k \le 29$
	$-20 \le l \le 21$	$-20 \le l \le 21$	$-21 \le l \le 20$	$-22 \le l \le 20$
Restraints/parameters	21/1035	19/1128	0/857	0/834
Goodness of fit (F^2)	1.044	1.065	1.069	1.037
R indices ($I > 2\sigma(I)$)	$R1 = 0.0990$	$R1 = 0.0791$	$R1 = 0.0598$	$R1 = 0.0721$
	$wR2 = 0.2385$	$wR2 = 0.1999$	$wR2 = 0.1535$	$wR2 = 0.1743$
R indices (all data)	$R1 = 0.1543$	$R1 = 0.0860$	$R1 = 0.0772$	$R1 = 0.1189$
	$wR2 = 0.2642$	$wR2 = 0.2052$	$wR2 = 0.1642$	$wR2 = 0.2066$

J = 13.4 Hz, 2H), 5.91 (d, J = 9.8 Hz, 2H), 6.65—7.16 (m, 18H), 7.31 (t, J = 7.5 Hz, 1H), 7.51 (d, J = 7.5 Hz, 2H), 8.52 (s, 2H, OH), 8.61 (s, 2H, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 31.6 (t), 32.1 (t), 32.5 (t), 32.9 (t), 78.9 (t), 119.8 (d), 120.1 (d), 125.8 (d), 127.58 (s), 127.63 (s), 127.7 (s), 128.0 (s), 128.2 (d), 128.4 (d), 128.6 (d), 128.7 (s), 129.17 (d), 129.23 (d), 129.3 (d), 129.4 (d), 132.4 (d), 132.9 (s), 134.0 (s), 138.0 (s), 152.1 (s), 152.2 (s), 152.3 (s). Found: C, 73.14; H, 5.17; Br, 9.77%. Calcd for $C_{50}H_{41}BrO_6$: C, 73.44; H, 5.05; Br, 10.24%.

37,40-[2-Bromo-5-*t*-butyl-1,3-phenylenebis(methyleneoxy)]-calix[6]arene-38,39,41,42-tetrol (2b). Prepared from **4** and **5b** by the procedure similar to that for **2a** in 86% yield.

2b: Colorless crystals (from dichloromethane/ethanol), mp > 300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.17 (s, 9H, *t*-Bu), 3.20 (d, J = 13.4 Hz, 1H), 3.30 (d, J = 13.7 Hz, 1H), 3.59 (d, J = 13.4 Hz, 2H), 3.61 (d, J = 13.7 Hz, 2H), 3.90 (d, J = 13.4 Hz, 1H), 4.07 (d, J = 13.7 Hz, 1H), 4.33 (d, J = 13.4 Hz, 2H), 4.80 (d, J = 9.8 Hz, 2H), 4.89 (d, J = 13.7 Hz, 2H), 5.94 (d, J = 9.8 Hz, 2H), 6.64—6.76 (m, 4H), 6.97—7.15 (m, 14H), 7.63 (s, 2H), 8.55 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 30.9 (q), 31.7 (t), 32.3 (t), 32.5 (t), 32.9 (t), 34.5 (s), 79.2 (t), 119.6 (d), 120.1 (d), 124.5 (s), 125.8 (d), 127.3 (s), 127.7 (s), 128.0 (s), 128.2 (d), 128.6 (s), 128.7 (d), 129.2 (d), 129.27 (d), 129.32 (d), 129.4 (d), 130.0 (d), 133.0 (s), 134.1 (s), 137.5 (s), 151.1 (s), 152.2 (s×2), 152.4 (s). Found: C, 74.47; H, 5.79; Br, 9.02%. Calcd for $C_{54}H_{49}O_6Br$: C, 74.22; H, 5.65; Br, 9.14%.

Molecular Mechanics Calculations. All calculations were carried out with the MacroModel software package (version 6.5)[5] running on a O2 Silicon Graphics workstation. The energy was minimized using the MM3* force field after setting the solvent option to chloroform. A 10000-step Monte Carlo multiple-minimum conformational search on **1a** was performed starting from the cone conformation with C_{2v} symmetry to afford the pinched cone conformation as the global energy minimum structure. The local minimum structure of the half-pinched/half-winged conformation was obtained with the aid of the low mode conformational search algorithm.[18]

X-Ray Crystallographic Analyses. Single crystals of **1a**·5$CHCl_3$ and **1i**·5$CHCl_3$ were grown in their chloroform solution. The intensity data were collected at 150 K (**1a**) and 120 K (**1i**) on a MAC Science DIP-2030 imaging plate area detector with Mo $K\alpha$ radiation (λ = 0.71069 Å). Reflection data were corrected for Lorentz and polarization factors, and for absorption using the multi-scan method. Crystallographic and experimental data were listed in Table 3. The structures were solved by the direct method and refined by full-matrix least squares on F^2 using SHELXL 97.[19] The non-hydrogen atoms were refined anisotropically except for the minor component of the disordered bridging unit (0.90 : 0.10 for **1a** and 0.93 : 0.07 for **1i**) and hydrogen atoms were idealized by using the riding models.

Single crystals of **1c**·CH_3CN·C_6H_6 and **1d**·CH_3CN·C_6H_6 were grown in their benzene/acetonitrile solution. The intensity data were collected at 120 K on a MAC Science DIP-2030 imaging plate area detector with Mo $K\alpha$ radiation (λ = 0.71069 Å). Reflection data were corrected for Lorentz and polarization factors, and for absorption using the multi-scan method. Crystallographic and experimental data are listed in Table 3. The structures were solved by the direct method and refined by full-matrix least squares on F^2 using SHELXL 97.[19] The non-hydrogen atoms were refined anisotropically and hydrogen atoms were idealized by using the riding models.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 145339-145342. The details of structures have been deposited as Document No. 73043 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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